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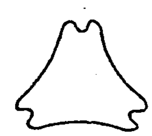
(54) Grooved fibre of irregular thickness.

(57) A thick and thin fibre has at least two axially-continuous grooves per filament with the entrance widths of the grooves lying between 0.2 and 4 μm and the depths between 0.1 and 1.8 μm. Such a fibre is made by dissolving out the easily-soluble polymer from a drawn composite fibre comprised of two thermoplastic polymer components having different solubilities. The fibre is of a silky nature and knitted and woven fabrics made therefrom have properties characteristic of silk fabrics.

Fig 1 (A)



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"GROOVED FIBRE OF IRREGULAR THICKNESS"

The present invention relates to a thermoplastic polymer fibre having variations of gauge or thickness along its length, the filaments being provided with axially-extending grooves. A specific intention is to provide a fibre which will give properties characteristic of silk fibres and knitted and woven fabrics made therefrom. In particular the invention aims to provide a fibre for producing an advanced silky knitted or woven fabric with a scroopy handle, an excellent lustre, colour depth, bulkiness and a natural irregularity.

A variety of modified shaped fibres are obtainable by making a composite fibre from two differently-soluble thermoplastic polymers and then dissolving out the more easily soluble polymer located in the vicinity of the surface of the fibre, either before or after making a fabric therefrom. For example the inventors proposed in Japanese Patent Laid-Open No.93819/1980 that a modified shaped fibre with a large degree of shape modification be obtained by dissolving out an easily-soluble polymer from a plurality of locations isolated by a relatively-insoluble polymer from a composite fibre. Such a fibre and knitted or woven fabrics mad therefrom are, however, liable to glitter lustre and decrease in colour depth, although a scroopy handle

can be given. Moreover the knitted or woven fabrics lack the bulkiness, natural irregularity and other properties specific to advanced silky knitted and woven fabrics.

Japanese Patent Laid-Open No. 53210/1981 also disclosed that a modified shaped fibre is obtainable by dissolving out an easily-soluble polymer located at specific points in the vicinity of the surface. It however has similar faults.

Japanese Patent Laid-Open No. 112535/1981 proposes a fibre having more than six axially-continuous grooves with widths of 0.1 to 4 µm, depths of 2 to 10µm and a high water absorption property. Such a fibre is also faulty in that its colour depth is not good because of the deep grooves, and bulkiness, natural irregularity and other properties are not given.

Further the inventors propose in Japanese Patent Laid-Open No. 5912/1982 and Japanese Patent Laid-Open No. 5921/1982 a thread having a scroopy handle, an excellent lustre, and grooves on the surface. It is obtained with tapering recesses formed at the transverse cross-section by dissolving out an easily-soluble polymer located in the vicinity of the vertices of its multilobal shape. Its knitted or woven fabric tend to show no satisfactory bulkiness and a monotonous appearance characteristic of the synthetic fibres.

Silky synthetic fibres are aimed at attaining the same characteristics as silk itself. The fabrics of silk however differ considerably from the knitted and woven fabrics of ordinary modified shaped polyester multi-filament fibres in the degree of scroopy handle, bulkiness and irregularity. Its fabrics become bulky when spaces are formed among fibres by removing sericin in their production process while polyester multi-filament fibres successfully become bulky when a thermal-shrinkage mixed yarn is made. The latter's manufacturing process however is complicated and involves a heavy cost. Further, silk fabrics have a characteristic appearance not attained by conventional synthetic fibres because their multi-filament fibres have a random irregularity in thickness along their axis. According to the measurement by a method to be described later, they have Uster Evenness values of 1 to 3% with 10 to 30 and 0 to 5 peaks every 50 m of Uster Evenness values of 4 to 10% and above 10% respectively.

A number of processes have been proposed for giving an irregularity in thickness to polyester multi-filament yarns through their irregular draw. Most of them form clearly distinctive thick and thin sections along the axis and this gives a clear difference of colour shade when dyed. These material yarns for advanced knitted and woven fabrics are not always

satisfactory because of their large Uster Evenness values of 5 to several ten %.

Japanese Patent Publication No. 7207/1976 discloses a polyester multi-filament fibre having more than three less-than-3cm long dispersed undrawn sections every 10cm thereof and elongations of 35 - 70%. Such fibres are however faulty in that they show a considerable difference of physical properties, particularly of large Uster Evenness value, between the thick and thin sections, because their low-speed spinning yarns are irregularly drawn, and a considerable difference of colour shade when dyed. They are susceptible to variation of the tension in their textile process because of their large elongations.

Further Japanese Patent Laid-Open No. 116819/1980 discloses a thick and thin yarn obtained by a process consisting of composite spinning a core component of polyethylene terephthalate and a sheath component of a mixture of polyethylene terephthalate and an ionic dyeable polyethylene terephthalate copolymer and drawing this composite fibre at a temperature less than 75°C. This too is not satisfactory as a material for advanced silky knitted and woven fabrics because it is aimed at producing varied dyeability effects and a clear difference of colour shade between the thick and thin sections and cannot be provided with any excellent lustre.

As described heretofore, the prior art methods have not succeeded in obtaining any material yarn capable of providing at the same time a scroopy handle, a crisp hand, a rustle, an excellent lustre, a colour depth, a bulkiness and natural irregularity specific to advanced silky knitted and woven fabrics.

An object of the invention is to provide a material yarn capable of presenting at the same time a scroopy handle, a crisp hand, a rustle, an excellent lustre, colour depth and bulkiness, and a natural irregularity specific to advanced silky knitted and woven fabrics, and a process for manufacturing the same.

In one aspect the invention provides a thermoplastic polymer fibre being thick and thin along its axis and having at least two axially-continuous grooves with entrance widths of 0.2 to 4μm and depths of 0.1 to 1.8μm per filament.

Another aspect of the invention provides a process suitable for producing the above mentioned fibre. Therein the grooves with the entrance widths of 0.2 to 4μm and depths of 0.1 to 1.8μm are formed by dissolving out at least part of an easily-soluble polymer having at least two locations with widths of 0.2 to 4μm at the periphery of the transverse cross-section from an axially thick and thin drawn composite fibre yarn comprised of two differently-soluble thermoplastic components.

Various aspects of the invention will now be further described by reference to the accompanying drawings, in which :

Figures 1(A) and 2 show representative transverse cross-sections of two forms of fibre in accordance with the invention;

Figure 1(B) is the transverse cross-section of the fibre of Fig. 1(A) showing in broken lines the assumed shape of the fibre if it had no grooves on the surface;

Figure 3 is an enlarged partial view of the transverse cross-section illustrating the shape of the grooves.

Figures 4 and 5 show examples of the transverse cross-sections of the composite fibre in accordance with the invention;

Figure 6 shows a stress-strain curve illustrating the elongation at the natural draw zone.

Figure 7 is a sketch of fibre bulkiness measuring equipment.

Figure 8(A), (B) and (C) are sketches illustrating fibre bulkiness measuring methods.

One of the features of the fibre in accordance with the invention is the shape of the axially-continuous grooves. It will be described hereinafter in connection with the drawings. Figures 1 (A) and 2 show examples of the preferred transverse cross-sections of a fibre having grooves on the surface.

The former has three grooves formed at almost equal intervals at the periphery. A transverse cross-section, assumed to be without grooves, shown in Figure 1(B) in broken lines, has a trilobal shape of which grooves are formed in the vicinity of the vertices. The cross-section of Figure 2 shows five grooves formed at almost equal intervals at the periphery. The transverse cross-section without grooves would have a pentalobal shape and the grooves are formed in the vicinity of the vertices.

Figure 3 exemplifies the shape of the grooves of a fibre. The entrance width is the length of the common tangent PQ across the vicinity of the groove and the depth is a line segment interconnecting the centre S of the common tangent PQ and the point R closest to the centre of gravity on the surface of the groove. The invention requires the entrance width to be 0.2 to 4μm and depth to be 0.1 to 1.8μm. If the former is beyond the limits given, no or a very small improvement is found in colour depth. Preferred ranges are 0.3 to 3μm, more preferably 0.4 to 2 μm.

The shape of the grooves is expressed in terms of the mean value obtained by measuring all of them on 20 filaments selected at random. Their depth is preferably within the range 0.2 to 1.6μm. A scroopy handle is obtainable when the depth is greater than about 0.2 μm, and an increase in depth

improves this scroopy handle. The improvement in colour depth, on the other hand, is zero or very small when the depth of the groove is less than 0.1 μm, becomes small again when the depth is increased above about 1 μm and becomes very small when it is greater than 1.8 μm. It is necessary to provide at least two grooves and preferably more than two grooves per filament in accordance with the invention. In case of one groove per filament, the probability of its presence on the surface is too low for a considerable improvement in colour depth and scroopy handle on the fabric made of the fibre. It is however preferable to provide less than 15 grooves and more desirable that there shall be 3 - 12 grooves. On the other hand the surface of the other parts than grooves of the fibre decreases in lustre. In Figure 3 M is the centre of the line $\overline{SR}$ and the orthogonal line to SR passing through M intersects the faces of the groove at T and U. For preventing glitter and for an improvement in colour depth with a decrease of the reflection from the faces PT and QU, it is preferable that the length of line segment $\overline{TU}$ corresponds to 40 - 90% of that of line segment $\overline{PQ}$, and this results in grooves tapering toward the centre of gravity of the fibre. For providing an excellent lustre, it is preferable that the sum of the lengths of the line segments $\overline{PQ}$ of the grooves shall be 2 to 40%, more preferably 5 to 35%, of the peripheral length of the fibre excluding the grooves.

A modified shape effect can be produced, particularly a silky lustre can be given, by modifying the transverse cross-section where no groove is assumed to be present. All known modified shape sections are applicable to the invention. For providing a silky lustre, however, the fibre is preferably required to have a T-type or 3 - 6 lobal shape. For considerable improvement in scroopy handle and colour depth, it is preferable to locate at least one groove in the vicinity of a vertex of the modified shape section, though it is not always necessary to locate grovoes in the vicinity of all the vertices of the modified shape section. However it is desirable to locate the grooves in the vicinity of the majority of the said vertices, and more preferable that grooves be located in the vicinity of all the vertices. It is preferred not to locate grooves on the recessed face between the vertices of the modified shape section because fibrillation is liable to occur. The assumed transverse cross-section without a groove is that of the fibre surface across line segment $\overline{PQ}$ without the face PTRUQ. The vertices of a modified shape section are the points most distant from the centre of gravity of fibres on the outwardly-raised surface and the wording "present in the vicinity of the vertices" means "present at and around the vertices".

The form of the side faces of grooves and the other parts is not limited. For an improvement

in colour depth, however, it is preferable to provide more than five recesses per 10 μm as seen at right angles to the fibre axis, these having widths of 0.1 to 1μm and lengths less than 5μm along the axis of a fibre produced by treating a polyester fibre with an aqueous alkaline solution.

It is not desirable to form a number of streaky concave and fine concave-convex surfaces because a decrease occurs in lustre. For an increase in colour depth without any noticeable decrease in lustre, however, it is preferable to form streaky concave and fine concave-convex surfaces on only the faces of grooves.

The fibre having grooves on the surface in accordance with the invention is characteristic of being thick and thin along its axis. For providing an irregularity similar to that of silk, the Uster Evennness value obtained by the measuring method to be described later can be fixed at 0.7 to 2.5% and it is more preferable to fix it at 0.9 to 2.2%; it is preferable to fix the number of the peaks within the Uster Evennness Value range of 4 to 10% at 5 to 80 every 50m, more preferably at 10 to 50; and it is furthermore preferable to fix the number of the peaks within the Uster Evennness Value range above 10% at less than 10 every 50m. It is not desirable to fix the Uster Evennness Value above 3% because a difference of internal structure between

the thick and thin sections causes a considerable difference of dyeing degree to result in so-called thick and thin yarn that does not provide a silky appearance.

A fibre having the Uster Evenness values of 0.7 to 2.5% and being thick and thin is susceptible of a natural irregularity, a bulkiness and a good colour depth. Bulkiness can be expressed in terms of the bulkiness degree to be obtained by applying a measuring method to be described later. It is desirable for the degree of bulkiness to be more than 10cc/gr., more preferably above 12cc/gr. Such a bulkiness effect on the knitted and woven fabric can cause an improvement in colour depth. The reason for this is not definitely known but is considered to be the trap effect of the incident light to the surface of knitted and woven fabric by the clearances among the filaments. In the case of the yarn being thick and thin and having grooves on the surface in accordance with the invention, it is considered that their specific shape, thickness and thinness, and the clearances among the filaments can effect a considerable improvement in colour depth.

The invention also provides a process for producing a fibre which is thick and thin and has grooves on the surface, which is characterized in that grooves with entrance widths of 0.2 to 4μm and depths of 0.1 to 1.8μm are formed by dissolving out part of the easily-soluble polymer having at least two locations with

widths of 0.2 to 4 μm at the periphery of the transverse cross-section from a drawn composite fibre yarn which is comprised of two differently-soluble thermoplastic polymer components and which is thick and thin along its axis.

An undrawn composite fibre suitable for the manufacture of the thick and thin fibre of the invention is obtainable by applying the processes which the inventors previously proposed in Japanese Patent Laid-Open No.5912/1982 and Japanese Patent Laid-Open No. 5921/1982.

It is preferable that the speed of spinning the composite fibre be between 2,000 and 4,000m/min. and more preferable to between 2,500 and 3,500m/min. If the spinning speed is below these values, only a low-tenacity thick and thin fibre is producible and a silky irregularity is difficult to obtain because an excessive difference arises between thickness and thinness. If the spinning speed is greater than the above values, thickness and thinness are too small to obtain a silky irregularity.

Conventional drawing apparatuses are applicable to the low draw-ratio draw of the composite polyester fibre for obtaining the thick and thin drawn fibre. Particularly in the case of composite polyester fibres, the combination between hot pins and hot plates or betweer hot rollers and hot plates is preferable for forming thickness and thinness steadily along the axis

although it is not necessary if a proper quantity thereof are installed between the rollers for the feed and constant draw-ratio take-up at a constant speed. For obtaining the thick and thin drawn yarn, the chosen draw-ratio should preferably be below (1 + elongation at natural draw zone x 2.2). It is preferable to choose the draw-ratio between(1 + elongation at natural draw zone x 1.1) and (1 + elongation at natural draw zone x 2.2) for establishing an Uster Evenness Value of the drawn thick and thin yarn at 0.7 to 2.5% and that of the fibre having grooves on the surface at 0.7 to 3.0% and between(1 + elongation at natural draw zone x 1.3) and (1 + elongation at natural draw zone x 2.0) for establishing it at 0.9 to 2.5%, and more preferable to cause the yarn to be drawn with the draw-ratios of between(1 + elongation at natural draw zone x 1.4) and(1 + elongation at natural draw zone x 2.0) in order to present no elongation at the natural draw zone at its S-S curve, show elongations of 20 to 35%, present a proper irregularity, improve in textile process passability and become unsusceptible of the variation of the tension in the textile process. Draw start temperature T (C°) should preferably be fixed in a range calculated by using expression :

$$T \leqq \frac{30+143\text{x(Elongation at natural draw zone)} - 30\text{x(Draw-ratio)}}{1.1\text{x(Elongation at natural draw zone)}}$$

for establishing at 5 to 100 every 50m the number of the peaks within the Uster Evenness Value range of

4 to 10% of the thick and thin drawn yarn suitable for establishing that of the fibre having grooves on the surface at 5 to 80 every 50m.

The shrinkage in boiling water of the drawn yarn by the combination between hot pins and hot plates or between hot rollers and hot plates is controllable by means of hot plate temperature. A hot plate temperature of 100 - 160°C is preferable to produce a boiling water shrinkage of 4 - 18% which is suitable for the composite polyester fibre. It is also effective for overcoming a tendency of the woven or knitted fabric of an ordinary thick and thin yarn to cause a crepe when dyed.

The thick and thin composite fibre can be made increasingly bulky. It is preferable for the degree of bulkiness to be above 10cc/gr. and more preferably above 12cc/gr. Next, consideration will be given to the shape at the transverse cross-section of the thick and thin composite fibre. Figure 4 shows a 2-component composite fibre trilobal shape yarn whose easily-soluble polymer B has three locations isolated by relatively-insoluble or insoluble polymer A in the vicinity of vertices of the section. The easily-soluble polymer on the surface of such 2-component composite fibres as seen in cross-section is required to have the lengths of 0.2 to 4μm and form grooves with the entrance widths of 0.2 to 4μm and the depths of 0.1

to 1.8μm when at least part thereof is dissolved out. The length corresponds to that of the line segment interconnecting the boundary points between it and the relatively-insoluble or insoluble polymer on the surface. If it is smaller than 0.2μm or larger than 4μm no or a very small improvement can be made in colour depth when grooves are formed by dissolving out at least part of the easily-soluble polymer. It should preferably be from 0.3 to 3μm and more preferably from 0.4 to 2μm. It is preferable that the sum of the lengths of the easily-soluble polymer should be 2 to 40% of the peripheral length of the other polymer and more preferably 5 to 35% of the same for providing an excellent lustre when a fibre having grooves on the surface is obtained by dissolving out at least part of the easily-soluble polymer. Such a fibre having grooves on the surface as shown in Figure 1 is producible by dissolving out the easily-soluble polymer from such a 2-component composite fibre as shown in Figure 4. The locations of the easily-soluble polymer are not limited in the fibre. They may be satisfactory deep in the fibre or the easily-soluble polymer having the deeper locations may be combined. However it should be preferably made tapering inwardly of the fibre. As described hereinbefore, it is particularly preferable to locate the easily-soluble polymer so that the length of line segment $\overline{TU}$ corresponds

to 40 to 90% of that of line segment $\overline{PQ}$ and grooves are shaped tapering toward the centre of the fibre when the fibre having grooves on the surface is obtained by dissolving out at least part of the easily-soluble polymer. Further it is preferable from the standpoint of the steady spinning of the composite fibre to make the easily-soluble polymer symmetric with respect to the rotation axis passing the centre of gravity of the fibre.

A modified-shape transverse cross-section effect can be produced, particularly a silky lustre can be provided, for the composite fibre in accordance with the invention by giving a modified shape transverse cross-section to the aforementioned composite fibre. All known modified shaped transverse cross-sections are applicable. For providing a silky lustre, however, it is preferable to select a T-type or 3- to 6-lobal transverse sections. The invention ensures a considerable improvement in colour depth and scroopy handle when specific grooves aforementioned are formed by dissolving out at least part of the easily-soluble polymer whose surface forming part is located in the vicinity of the vertices of a modified shape transverse cross-section from the composite fibre.

Now consideration will be paid to the easily-soluble polymer and to the relatively insoluble or insoluble polymer covering all or the greater part

of the fibre having grooves on the surface. They may be properly selected from known thermoplastic polyamides, polyesters and polyolefins in connection with the solvent to be used. If immiscible polymers are used in combination, however, separation occurs therebetween so that fuzz, fibre break and so forth are liable to take place in fibre-manufacturing and textile processes. it is therefore preferable to select a combination of miscible polymers. The term "miscible" means that no substantial separation is observed in the drawn composite fibre.

A preferred relatively-insoluble or insoluble type of polymer is polyester, which is superior in physical and chemical properties, extensively used for clothing, and ensures a considerable improvement in colour depth. As regards the methods for dissolving out the easily-soluble component from the composite fibre, it is preferable to select an aqueous alkaline solution in view of its facility of operation, safety and cost. From this standpoint, the easily soluble polymer should preferably be selected from alkali-soluble polymers. Easily-alkali-soluble polymers include the copolymers or blendings between polyester and polyalkyleneglycol derivatives, anionic-surfactant-added polyesters, and the blendings between the polyesters containing metal sulphonate groups and polyesters, or the polyesters containing metal sulphonate groups.

Among the easily-soluble polymers the blendings between the polyesters containing metal sulphonic groups and polyesters or the polyesters containing metal sulphonate groups are preferable for their easy uniform dissolving out of the composite fibre. particularly preferable among the polyesters containing metal sulphonate groups are 5-sodium-sulphiosophthalate (1 to 10 mole %) / ethyleneterephthalate (99 to 90 mole %) copolymer polyester.

The fibre having grooves on the surface in accordance with the invention is not obtainable unless the ratio of dissolution speed of the easily-soluble polymer to the relatively-insoluble or insoluble polymer is more than 1. It should be fixed preferably above 1.5 and more preferably above 2. Particularly it should be fixed preferably at 1.5 to 8 and more preferably at 2 to 6 for the aqueous alkaline solution treatment most suitable for dissolving out at least part of the easily-soluble polyester from the composite fibre in accordance with the invention. it is preferable to form a certain number of recesses with widths of 0.1 to 1 μm and lenghts less than 5 μm along the axis at the rates of more than five to a maximum of 10 orthogonally with the axis on the surface of the fibre formed through the aqueous alkaline solution treatment of an ordinary polyester fibre on the side faces of the other parts than the grooves on the

surface of the fibre by dissolving out more than 6% of the relatively-insoluble polyester.

The composite-fibre forming thermoplastic polymer may contain such amounts of delusterants, antioxidants, fluorescent brighteners, ultraviolet absorbers and other additives as do not affect the good properties of the fibres of the invention.

The composition ratio by weight of the easily-soluble polymer to the relatively-insoluble or insoluble polymer preferably lies between 2:98 & 30:70 and more preferably between 5:95 & 20:80, thereby obtaining the fibre having grooves on the surface through dissolving out all the easily-soluble polymer, for ensuring the uniform dyeing of the fabric.

The fibre having grooves on the surface in accordance with the invention is preferably a filament type one with 0.5 to 10 denier suitable for ordinary clothing. It is usable in the form of denier mixes, thermal shrinkage mixes and cross-section shape mixes, or after mixing with the other fibres.

Although the composite fibre may be alkali-treated prior to weaving or knitting, the composite fibre should preferably be alkali-treated after weaving or knitting.

The fabric, so alkali-treated after being woven or knitted, is more bulky and exhibits a softer hand as compared with the fabric woven or knitted

from alkali-treated fibres, because clearances among the filaments are formed thereamong. Furthermore, the efficiency of an alkali-treated treatment is greater after weaving or knitting than before weaving or knitting. In the case where the fabric is alkali-treated after being woven or knitted, it is preferable that the fabric be, prior to the alkali-treatment, subjected to scouring and then a dimensional stabilization heat treatment under conditions such that no crepe defect occurs in the fabric.

An aqueous alkaline solution is preferable for dissolving-out treatment as described hereinbefore. The alkali-treatment of the fibre or fabric is generally carried out by using a jigger, a wince, a beam, a suspended tank or any other known means.

In order to enhance dissolution of the soluble polymer component, an additive, such as a phenol compound, an amine compound, a quaternary ammonium salt or a high-boiling point polyhydric alcohol, may be incorporated in the aqueous alkaline solution. Among alkaline metal hydroxides, sodium hydroxide is preferable in view of its low cost and enhanced capability for dissolution of the soluble component. The aqueous alkaline metal hydroxide solution is used, preferably, at a concentration of from 0.5 to 20% by weight and the temperatures from 70 to 120°C.

As described herebefore, the fibre being thick and thin and having grooves on the surface in accordance with the invention is suitable as the material yarn of the advanced silky woven or knitted fabric having a scroopy handle, an excellent lustre, a colour depth, bulkiness and a natural irregularity. Its manufacturing process may be used without any special systems or conditions.

Hereinafter the invention will be described in further details in connection with its examples. The methods of measuring elongation at natural draw zone, Uster Evenness Value, bulkiness degree and colour depth follow.

Elongation at natural draw zone.

A graph such as shown in Figure 6 is obtained by using an instron tensile tester and the elongation of C is read. For example "40%" is "0.4".

Uster Evenness Value %.

Normal test measuring is carried out using a commercially-available Uster Evenness Tester (manufactured by Keisokuki Kogyo K.K.) during the twisting at about 1,500 rpm effected by a twister with a measuring slotter selected in accordance with the total denier of the yarn and its speed fixed at 25m/min. Uster Evenness curves are to be drawn at a chart speed of 5cm/min and a range of ± 12.5%. The accessory integrator is used to read the Uster Evenness Value

in terms of the value of the irregularity of the yarn for three minutes. Three minutes' measuring is carried out at least five times and Uster Evenness value is expressed in terms of its mean value.

The number of Uster Evenness Value peaks is obtained by reading their size in terms of the difference between their upper and lower ends on the aforementioned measuring chart. At least five measurings are obtained for 50m and their mean value is calculated.

<u>Degree of bulkiness.</u>

A perspective view of a device for measuring the degree of bulkiness is shown in Figure 7 and that of the method of the measuring thereby in Figure 8. This device comprises a sample table 10 which has an upper plate with a pair of spaced apart parallel openings 15. The spacing 16 between the outside edges of the openings 15 is selected to have a length of 6mm. An upper end of a flexible tape 11 having a width of 2.5cm made of a thin fabric is positioned to loop around the openings 15. A member 12, which is provided with an indicator needle and a weight 13, is secured to the lower end of the tape 11. A scale 14 is positioned so that the needle of the member 12 indicates zero (cm) when no sample is placed on the table 10.

Samples in the form of hanks each having 80 windings are prepared by using a reel which has a peripheral length of 1 meter. The number of hanks to be prepared should be between 2 and 10 in accordance with the yarn's denier number. The hanks which are hung in a no-load condition are subjected to heat treatment in the atmosphere at a temperature of $200 \pm 2°C$ for five minutes. Next, the heat-treated hanks are bundled together in parallel so that the total denier is equal to 48,000. (For example, when a yarn of 30 denier is used, $30 \times 80 \times 2 = 4,800$, and therefore $48,000 \div 4,800 = 10$ hanks; when a yarn of 75 denier is used, $75 \times 80 \times 2 = 12,000$, and therefore $48,000 \div 12,000 = 4$ hanks.) The parallel bundled hanks are folded into four parts as shown in Figure 8(A) to form a sample 17. The sample 17 is inserted between the tape 11 and the sample table 10 as shown by Figure 8(B) front view and Figure 8(C) sectional view. Needle indication L(cm) is read with the weight 13 so controlled that the total weight of it and the member 12 is fixed at 50 gr. Three different values L are measured by changing the position of the sample 17. Next, a mean value $\overline{L}$ (cm) of the values L is calculated. The degree of bulkiness M is calculated from the following equation;

$$M\ (cc/g) = \frac{\text{Volume of the yarn (V)}}{\text{Weight of the yarn (W)}} = \frac{V}{W}$$

$$V = \frac{(\bar{L})^2}{\pi} \times 2.5$$

$$W = D \times \frac{100}{100 - SH} \times P \times 0.025 \times \frac{1}{9{,}000}$$

wherein D is the denier of the yarn before heat treatment; P is the number of the filaments in the yarn; and SH is the shrinkage (%) in dry heat, which is obtained by measuring, before and after the heat treatment, the lengths of the hanks under a load of 0.1 gr./d.

Depth of colour.

A fabric comprised of a fibre sample to be measured was subjected to a normal method of scouring in the boiling water containing 0.2% of nonionic surfactant "Sandet" G-900 (manufactured by Sanyo Chemical Ind.Ltd.) and 0.2% of soda ash for five minutes,rinsing in water, drying and dyeing.

The dyeing was continued for 60 minutes in a 130°C aqueous solution with a bath ratio of 1 to 30 of 10% owf of disperse dye Sumikaron Black S-3B, 0.5cc/lit. of acetic acid and 0.2 gr./l of sodium acetate. Thereafter it was subjected to an ordinary method of reductive washing in an 80°C aqueous solution of 2 gr./l. of hydrosulphite., 2 gr./l. of caustic soda, 2 gr./l. of the non-ionic surfactant (Sandet G-900) for 20 minutes, drying and 200°C dry heat treatment for five minutes.

The depth of colour was measures in terms of the L-value by using a colour computer AUD-SCH-2 Type (manufactured by Suga Test Instruments Co.,Ltd.) with more than five pieces of the fabric put one upon another so that no radiant light transmitted them. The L-value decreases or increases with the increase or decrease respectively in depth of colour.

Example 1:

An undrawn yarn having 24 filaments with 120 denier and an elongation at natural draw zone of 42% was obtained through melt-spinning by using a composite spinning apparatus of 5-sodium sulphoisophthalate (1.6 mole %) - ethyleneterephthalate (98.4 mole %) copolymer polyester (intrinsic viscosity in25°C orthochlorophenol - 0.54, containing 0.2% of titanium oxide) as easily-soluble polymer and polyethylene terephthalate (intrinsic viscosity - 0.65, containing 0.03% of titanium oxide) as relatively-insoluble polymer at a temperature of 295°C and at a spinning speed of 3,000m/min. The ratio of dissolution speed between the polymers was 3.4 in terms of the dissolution condition to be described later. The yarn was drawn at a rate of 300m/min. and at a draw-ratio of 1.7 with the temperature of hot pin fixed at 60°C and that of hot plate fixed at 120°C so that a drawn yarn having such a sectional shape as shown in Figure 5 and being thick and thin was

obtained. It showed a 1.2 μm width on the surface of the fibre of the easily-soluble polymer, 4.8 μm distance thereof between the points closest and most distant to the centre of gravity, 32% elongation with the substantial absence of that at natural draw zone at S-S curve, 11% shrinkage in boiling water, 21cc/g degree of bulkiness, 1.4% Uster Evenness Value and 21 peaks/50m at the range 4 to 10%.

A 28G single jersey knit of a thick and thin drawn yarn was subjected to scouring 160°C intermediate setting and 80°C treatment with an aqueous alkaline solution of 30 g /lit. of NaOH for different time periods to produce a fibre having the depths shown in Table 1 on the surface. All the obtained samples thereof showed the groove entrance widths of 1.2 to 1.4 μm, 70 to 85% ratios of the line segment TU shown in Figure 3 to the entrance widths, 1.1 to 1.3% Uster Evenness Values, and 12 to 18/50m peaks at 4 to 10% Uster Evenness Values.

Table 1.

Run No.	1(Comparative example)	2	3	4	5	6	7(Comparative example)
Groove depth	0.08	0.1	0.3	1.0	1.5	1.8	2.1
L-value	14.1	13.8	13.3	12.5	13.2	13.6	14.0

As shown in Table 1, a depth of colour was observed in the samples of Run Nos.2 to 6, of which that of Nos. 3 to 5 was good. The scroopy handle

increased with the increase in depth of grooves. No.2 showed a scroopy handle and No. 3 a distinct scroopy handle. Excellent lustre, bulkiness and natural irregularity were almost equal for all the samples.

Comparative example 1:

A drawn yarn substantially without thickness and thinness was obtained by drawing the undrawn yarn of Example 1 at a draw speed of 300m/min., a hot-pin temperature of 125°C, a hot-plate temperature of 120°C, and a draw-ratio of 1.93. It showed 0.44% Uster Evenness Value, 0 peak at more than 4% Uster Evenness Values, 8cc/gr. bulkiness degree and 25% elongation. The fabric knitted as Example 1 was subjected to alkaline aqueous solution treatment for obtaining a groove depth equivalent to that ot No. 4 of Example 1. The L-value level in depth of colour is 13.2, and the knitted fabric had a monotonous appearance and is not bulky despite a scroopy handle and an excellent lustre.

Example 2.

A fabric was knitted of a multifilament yarn that has one isolated part of the easily-soluble polymer at the transverse cross-section of the composite fibre made according to Example 1.

The above filament yarn is called Run No.8 sample corresponding to comparative example and the filament

yarn that has two isolated parts is called Run No.9; both were subjected to alkaline aqueous solution treatment for obtaining a fibre having grooves with an entrance width of 1.3 μm and a depth of 1.0 μm and being thick and thin. The ratio of the easily-soluble polymer to the relatively-insoluble polymer of the samples of Run Nos. 8 and 9 was fixed however at 5 to 95 and 10 to 90 respectively. The sample of Rune No.8, a thick and thin drawn yarn, showed 35% elongation, substantially no elongation at natural draw zone at S-S curve, 10% shrinkage in boiling water, 20cc/gr. degree of bulkiness, 1.5% Uster Evenness Value and 25 peaks/50m at 4 to 10% Uster Evenness Values. The sample of Run No.9, a thick and thin drawn yarn, showed 34% elongation, substantially no elongation at natural draw zone at curve S-S, 11% shrinkage in boiling water, 21cc/g degree of bulkiness, 1.6% Uster Evenness Value, 27 peaks/50m at 4 to 10% Uster Evenness Values. The sample of Rune No.8 exhibited an L-value of 13.9 and a shortage of scroopy handle while that of Run No.9 a L-value of 12.9 and a distinct scroopy handle. The samples of Runs Nos.8 and 9 of the fibre having grooves on the surface had 1.3% and 1.4% Uster Evenness Values and 22 and 25 peaks/50m at 4 - 10% Uster Evenness Values, and both their fabrics showed the same excellent lustre, bulkiness and natural irregularity as the sample of Run No.4.

Example 3.

A 120 denier - 24 filament undrawn composite fibre was made according to Example 1 and it was subjected to spinning, thick and thin drawing, knitting and aqueous alkaline solution treatment so that a fibre having grooves with a depth of 1.0 μm on the surface was obtained.

Therein the spinning output ratio ofeasily-soluble polymer and relatively-insoluble polymer was properly varied for obtaining the specified entrance width at the transverse cross-section of the composite fibre as shown in Table 2 and draw-ratio was fixed at (1 + elongation at natural draw zone x 1.67). All the thick and thin drawn yarns showed 30 to 34% elongations, substantially no elongation at S-S curve, 10 to 12% shrinkages in boiling water, 19 to 22cc/g degrees of bulkiness, 1.4 to 1.6% Uster Evenness Values and 22 to 30 peaks/50m at 4 to 10% Uster Evenness Values. All the fibres having grooves on the surface had 65 to 88% ratios of the line segment TU shown in Figure 3 to the entrance widths. The colour depths observed in the sample fabrics of Runs Nos. 11 to 17 as shown in Table 2 were good for Nos. 12 to 16 and better for Nos. 13 to 15.. The samples of Run Nos. 11 to 17 displayed a good scroopy handle, an excellent lustre, a bulkiness and a natural irregularity.

Table 2

Run No.	10 (Comparative Example)	11	12	13	14 The same as No.4	15	16	17	18 (Comparative Example)
Entrance width (μm)	0.18	0.22	0.31	0.40	1.3	2.0	2.8	3.9	4.3
L-value	14.0	13.7	13.3	12.9	12.9	12.8	13.2	13.8	14.2

Example 4.

The same thick and thin drawn yarn as Example 1 was obtained by using the undrawn yarn at the draw-ratios shown in Table 3 and subjected to knittingand aqueous alkaline solution treatment. The characteristics are shown in Table 3. The samples of Runs Nos. 24 to 26 showed an elongation at natural draw zone at S-S curve and the shrinkages in boiling water of 9 to 15%.

The fibres having grooves with the depths of 0.9 to 1.1 μmand the entrance widths of 1.2 to 1.5 μmshowed the characteristics shown in Table 3, and 72 to 85% ratios of line segment TU to the entrance widths. The scroopy handle, excellent lustre, bulkiness and colour depth of all the woven fabrics of Runs Nos. 19 to 26 were good. The woven fabric of Run No. 19 showed a slight scroopy handle, that of No. 20 a gentle scroopy handle, that of No. 26 with a large Uster Evenness Value an excessive difference of colour shade, that of No.25 a slightly excessive difference of colour shade, and those of Nos.21 to 24

a good natural irregularity. Those with the larger Uster Evenness Values exhibited the better degrees of bulkiness and the better depths of colour.

Table 3

Run No.	Draw -ratio	Thick and thin composite fibre					Thick and thin fibre having grooves on the surface			
		Uster Evenness Value (%)	Number of Ustur Evenness value peaks/50m		Degree of bulkiness (cc/g)	Elongation (%)	Uster Evenness Value (%)	Number of Uster Evenness value peaks/50m		L-value
			4 ∿ 10%	Above 10%				4 ∿ 10%	Above 10%	
19	1.94	0.65	4	0	10	16	0.62	2	0	13.0
20	1.90	0.73	6	0	13	18	0.70	5	0	12.8
21	1.82	0.92	13	0	15	21	0.88	10	0	12.6
22	1.72	1.5	22	3	19	29	1.4	19	2	12.4
23	1.59	2.0	48	8	22	34	1.8	45	6	12.4
24	1.55	2.3	65	13	26	38	2.2	58	11	12.3
25	1.48	2.8	90	18	32	43	2.5	76	16	12.2
26	1.43	3.2	132	22	35	55	3.1	103	20	12.2

CLAIMS :

1. A thick and thin fibre having grooves on the surface, characterized by being comprised of thermoplastic polymers, and with at least two axially-continuous grooves per filament with entrance widths of 0.2 to 4 μm and depths of 0.1 to 1.8μm.

2. A fibre as claimed in Claim 1, wherein said thermoplastic polymer is a polyester.

3. A fibre as claimed in Claim 1 or 2, wherein the transverse cross section of the assumed shape of the fibre if it had no groove is modified in shape.

4. A fibre as claimed in Claim 3, wherein at least one groove thereof is present in the vicinity of the vertices of the modified-shape transverse cross section thereof.

5. A fibre as claimed in any of Claims 1 to 4, wherein the Uster Evenness Value thereof is 0.7 to 2.5%.

6. A fibre as claimed in Claim 5, wherein the Uster Evenness Value thereof is 0.9 to 2.2%.

7. A process for producing a thick and thin fibre having grooves on the surface, characterized in that grooves with entrance widths of 0.2 to 4 μm and depths of 0.1 to 1.8 μm are formed by dissolving out at least part of the easily-soluble polymer from a drawn composite fibre comprised of two differently-soluble thermoplastic polymer components, the easily-soluble one of said

components having at least two locations with widths of 0.2 to 4 μm at the periphery of the transverse cross section thereof and being thick and thin along its axis.

8. A process for producing a thick and thin fibre having grooves on the surface, as claimed in Claim 7, wherein the transverse cross-section of the drawn composite fibre yarn is modified in shape.

9. A process for producing a thick and thin fibre having grooves on the surface, as claimed in Claim 8, wherein at least a portion of the surface forming part of said easily-soluble polymer is located in the vicinity of the vertices of said modified shape transverse cross-section.

10. A process for producing a thick and thin fibre having grooves on the surface, as claimed in any of Claims 7 to 9, wherein said composite fibre of said easily-soluble polymer is shaped tapering inward thereof at the section.

11. A process for producing a thick and thin fibre having grooves, as claimed in any of Claims 7 to 10, wherein said composite fibre is comprised of two polyesters which are differently soluble in an alkaline aqueous solution.

12. A process for producing a thick and thin fibre having grooves, as claimed in any of Claims 7 to 11, wherein said composite fibre is formed thick and thin

along its axis by drawing a polyester undrawn composite yarn at a low draw-ratio.

13. A process for producing a thick and thin fibre having grooves, as claimed in Claim 12, wherein said composite fibre is obtained by drawing an undrawn composite polyester yarn at a draw-ratio less than (1 + elongation at natural draw zone of undrawn composite yarns x 2.2).

14. A process for producing a thick and thin fibre having grooves, as claimed in Claim 12, wherein said composite fibre is obtained by drawing an undrawn composite polyester yarn at a draw-ratio more than (1 + elongation at natural draw zone of undrawn composite yarns x 1.1).

15. A fabric made of a thick and thin fibre having grooves on its surface as claimed in any of Claims 1 to 6, or made by the method of any of Claims 7 to 14.

Fig 1 (A)

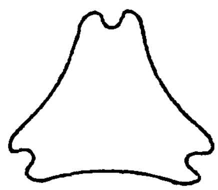


Fig 1 (B)

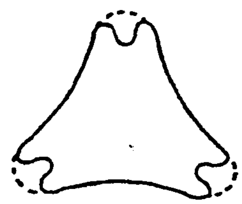


Fig. 2

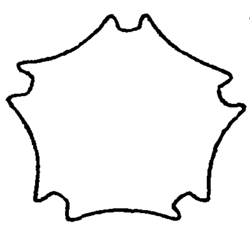


Fig. 3

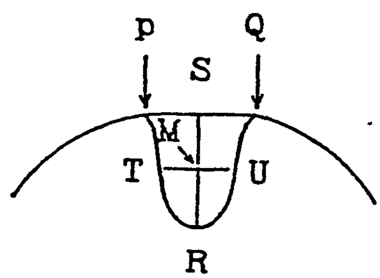


Fig. 4

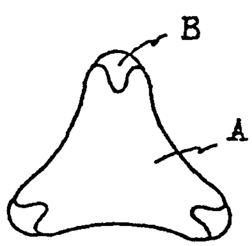


Fig 5

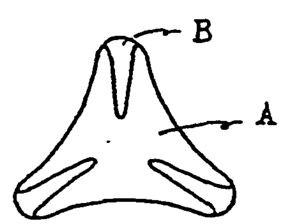


Fig 6

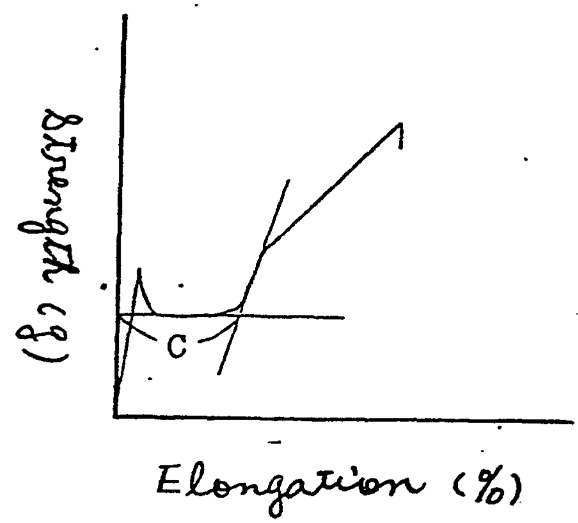


Fig. 7

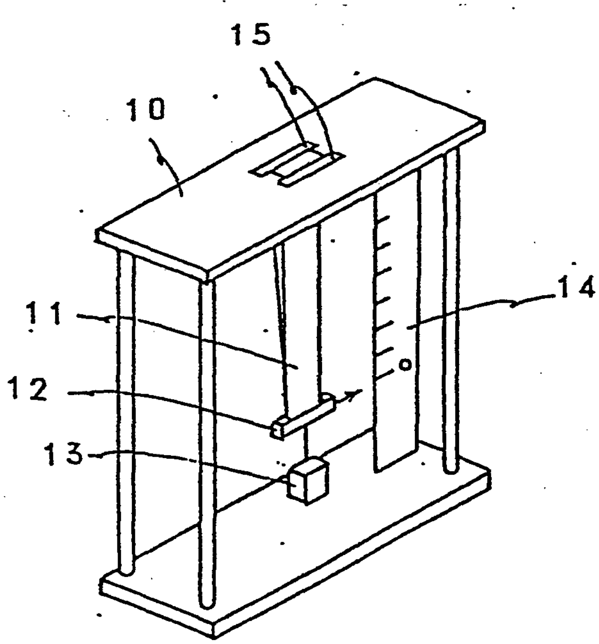


Fig 8 (A)

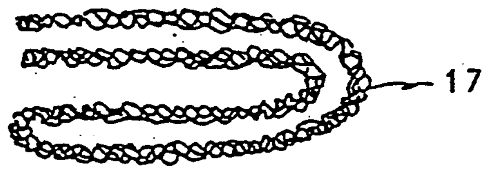


Fig 8 (B)

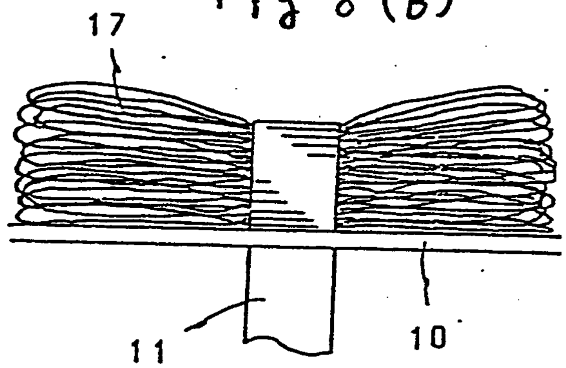
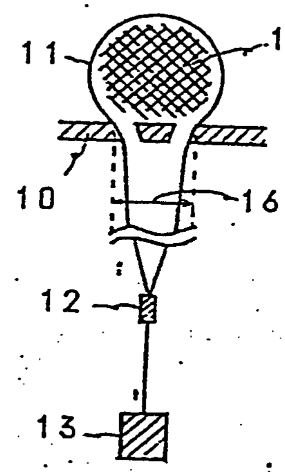


Fig 8 (C)



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(54) **Process for producing articles of regenerated chitin-chitosan containing material and the resulting articles**

(57) The present invention provides fiber materials, knits and textiles, nonwoven fabrics, miscellaneous daily goods or foam materials having an improved dyeability, bio-compatibility, anti-microbial activity, good biodegradative property, and being effective for deodorizing uses, growth enhancing uses for plants and medical uses, and having anti-microbial effect produced from the chitin-chitosan viscose which is produced by a xanthogenation reaction of alkaline chitin-chitosan having a different DAC ratio through a pre- and post-immersion steps in an NaOH solution, or from a viscose in which chitin-chitosan and cellulose are solubilized.

In the process for producing chitin-chitosan/cellulose fibers, films or foam materials from the chitin-chitosan/cellulose viscose, chitin-chitosan in which DAC ratio and degree of polymerization are adjusted is formed through an improved pre-immersion step in which the chitin material is immersed in a NaOH solution of high concentration at high temperature and through an improved post-immersion step in which the temperature is decreased. The chitin-chitosan/cellulose viscose is produced by a xanthogenation reaction with CS_2 and by dissolving in crashed ice. The viscose obtained or a viscose in which chitin-chitosan and cellulose are solubilized in a desired ratio is used for producing fibers or films, and the viscose in which a foaming agent is added is used for producing foam materials. Span-lace process nonwoven fabrics can be also produced from these viscose.

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Descripti n

Background of the Invention

(1) Field of the Invention

This invention relates to a process for producing a viscose of the material (referred to as chitin-chitosan hereinafter) having mixed structure units of chitin, which contains aminoacetyl groups, and of chitosan, which contains amino groups, on the same molecule by using chitin as a starting material. The invention also relates to clothing and the like having an improved dyeability, bio-compatibility, anti-microbial activity, and excellent bio-degradative property, such as fibers, knits and textiles, films, nonwoven fabrics, or foams composed of regenerated chitin-chitosan or a combination of regenerated chitin-chitosan and regenerated cellulose in various combination ratios which are obtained by spinning or foaming said chitin-chitosan viscose or a viscose in which said chitin-chitosn and cellulose are mixed in a desired amount or the viscose in which a foaming agent is mixed. The invention further relates to medical materials, hygienic materials, anti-microbial fibers, knits and texitiles, films, nonwoven fabrics, as well as miscellaneous daily goods made from these fiber materials, foam materials, and the like.

The term "bio-compatibility" herein implies, in addition to the common meaning, that the contact of chitin-chitosan containing material with human skin enhances the biological self-defensive function of the human body through lysozyme activities.

(2) Description of the Prior Art

Many attempts have been carried out to produce articles such as fibers, knits and textiles, films, nonwoven fabrics or foam materials using chitin or chitosan. The inventors of this invention have described details of the process for producing the aforementioned articles in Japan Patent Application HEI 6-252861 (referred to as the prior application of the inventors).

Summary of the Invention

Chitin or chitosan was simply processed to form fibers in the prior art and practical utilization of their characteristics was insufficient. Following the prior patent applications of the inventors, the inventors of this invention have investigated the art in detail and developed a process for producing articles of most desirable today having bio-compatibility, anti-microbial activity and improved dye affinity that has been a characteristic of the article, thus succeeding in its industrial production.

Chitin means β-1,4-poly-N-acetyl-D-glucosamine and the acetyl groups are eliminated and converted into amino groups in chitosan as a result of hydrolysis of chitin. Chitin having acetamide groups usually exhibits cell activation effects through various means in either animals or plants. It is utilized for human beings as healthy foods or medical materials in the forms of fibers, knits and textiles, films, nonwoven fabrics or foam materials. The effect for promoting chitinase production and the effect for improving the population of soil bacteria are also observed in chitin. Although evaluations for the effect of chitosan are indefinite, there often recognized that an increase of chitosan component enhances anti-microbial activity. We have also observed that the increase of chitosan component strengthens the anti-microbial effect of the articles.

In the continued investigation after completing the prior patent application by the investigators, it was reconfirmed that chitin-chitosan has cell activation effects and anti-microbial activity for all the livings including human beings. Moreover, it may be helpful for solving the worldwide problems of pollution of the earth through the adequate degradability and the ability of activating living cells. Based on the recognitions described above, we have completed the process for producing chitin-chitosan fibers or chitin-chitosan containing fibers and its articles.

According to the present invention, de-acetylation of chitin molecules is accomplished easily by loosening the highly tight tissue of chitin through a sodium hydroxide treatment at a high temperature range of 40°C or more to 95°C or less (pre-immersion step developed by the inventors). This process enabled to adjust the mixing ratio between chitin and chitosan (referred to as DAC ratio) in chitin-chitosan products to a most suitable value for the present invention. Thus, the invention succeeded in improving the industrial process for producing chitin-chitosan containing viscose. The present invention also made it possible for the first time to produce chitin-chitosan containing viscose in an industrial scale, thereby enabling the production of fibers, knits and textiles, films, nonwoven fabrics or foam materials that are useful for human beings. Fibers, knits and textiles, films, nonwoven fabrics or foam materials are generally termed as articles in this invention.

Detailed Description of the Invention

The first feature of this invention comprises a process for producing chitin-chitosan containing viscose characterized in that a chitin raw material containing 0.2% by weight or less of ashes, having a viscosity of 20 to 250 CPS and particle diameter of 4mm or less is used, comprising the steps of adjusting DAC ratio and degree of polymerization of said chitin material by immersing the material in 30 to 48% by weight of an aqueous solution of NaOH for 10 to 120 minutes at 40 to 95°C (referred to as a pre-immersion step) to form a compound having a structure unit of chitin having aminoacetyl groups and a structure unit of chitosan having amino groups (referred to as chitin-chitosan hereinafter), immersing the chitin-chitosan in said aqueous solution of NaOH for 10 to 60 minutes at a reduced temperature of 70 to 30°C to adjust NaOH content (referred to as a post-immersion step) and crushing the chitin-chitosan after compressing it into 3 to 5 times the specific weight of the chitin material; followed by subjecting to a xanthation of chitin-chitosan by introducing 30 to 80% by weight of CS_2 to the chitin material at 20 to 35°C for 2 to 4 hours at a lowered pressure, and then adding 2.5 to 30th volume of crushed ice to the chitin material to dissolve the chitin-chitosan with stirring for 2 to 30 hours.

The second feature of this invention comprises a process for producing a fiber of chitin-chitosan alone or a fiber composed of chitin-chitosan and cellulose, characterized in that the fiber is spinned by the wet spinning method for the conventional viscose rayon by using a viscose containing chitin-chitosan alone produced by the steps according to the first feature of this invention, or by using a viscose in which chitin-chitosan and cellulose are solubilized in a desired mixing ratio by weight.

The third feature of this invention comprises a process for producing chitin-chitosan films or chitin-chitosan and cellulose mixed films, characterized in that the films are formed by a conventional viscose process for producing cellulose films using a viscose of chitin-chitosan alone produced according to the process described in the first feature of this invention or using a viscose in which chitin-chitosan and cellulose are solubilized in a desired ratio by weight followed by defoaming.

The fourth feature of this invention comprises a process for producing foam materials of chitin-chitosan or mixed foam materials of chitin-chitosan and cellulose, characterized in that the chitin-chitosan viscose, which is produced by the process according to the first feature of this invention, or a viscose produced by the process according to the second feature of this invention, in which the chitin-chitosan and cellulose are solubilized in a desired amount, is mixed with a foaming agent and spinned in a spinning bath for the cellulose viscose to produce the foam materials.

The fifth feature of this invention comprises chitin-chitosan fibers or chitin-chitosan cellulose fibers, knits and textiles, films, nonwoven fabrics or foam materials, characterized in that fibers, films or foam materials composed of chitin-chitosan or chitin-chitosan and cellulose produced by the process according to the second, third or fourth step of this invention are used for clothing, hygienic articles or miscellaneous daily goods having bio-compatibility, anti-microbial activity and good dyeability.

The chitin-chitosan raw material used has an ash content of 0.2% or less, a viscosity of 20 to 250 CPS as measured at 30°C in a 0.4% solution of the material in N,N-dimethylacetamide/LiCl = 96/4, and a particle size of 4 mm or less in diameter. Fibers, knits and textiles, films, nonwoven fabrics or foam materials having bio-compatibility, excellent anti-microbial property and good dyeability are produced using the afore-mentioned chitin-chitosan material by the following processes.

(a) Pre-immersion in an alkaline solution: The chitin-chitosan material is subjected to an alkaline adduct process at a temperature range of 40°C to 95°C, which is a process found by the inventors for the first time and has not been used in the conventional process. A process comparable to the aging process in the rayon industry for adjusting the degree of polymerization of the chitin-chitosan material was made possible and the performance for filtration of the viscose obtained was improved by decreasing insoluble residues. The reason why this process is employed will be described hereinafter. The key point of this step is to loosen the texture of chitin-chitosan structure by treating at a high temperature, resulting in a finding that the following reactions are made easy to proceed. Thus, we have succeeded in producing fibers, knits and fabrics, films, nonwoven fabrics or foam materials having bio-compatibility, an excellent anti-microbial property and good dyeability by using the material according to the first feature of this invention by the process described above. When the ash content in the chitin material is more than 0.2%, the chitin-chitosan viscose produced contains large amount of unreacted particles which are hardly soluble and, when the viscosity is not in the range of 20 to 250 CPS or the particle size distribution is in the range of more than 4 mm, the solubility of the chitin-chitosan viscose is insufficient. In both cases, the material is not suitable for the viscose according to this invention and can not be used. Applying the pre-immersion step followed by the post-immersion step for the alkaline treatment of the chitin material enhances de-acetylation of chitin molecules, thereby making it possible to adjust the mixing ratio between chitin and chitosan (referred to as DAC ratio hereinafter) suitable for this invention in the range of 15 to 75%, preferably 18 to 70% and most preferably 25 to 70%.

(b) There are many reports describing that chitin is helpful for treating wounded portions of the body or effective for curing allergic diseases by making the human skin healthy through enhancement of the activity of lysozyme or

many other effects not defined yet. It has been made clear that chitosan is effective for the anti-microbial activity typically applied for clothing and miscellaneous daily goods. The afore-mentioned object of this invention is to adjust the DAC ratio described above to the desired value for the target of final products, thereby realizing an industrial production of fibers, knits and textiles, films, nonwoven fabrics and foam materials of chitin-chitosan or chitin-chitosan and cellulose. Without the pre-immersion and post immersion steps described above, the industrial production of various chitin-chitosan containing products is difficult, although they could be produced in laboratories. Articles such as fibers, knits and textiles, films, nonwoven fabrics or foam materials having bio-compatibility, excellent anti-microbial property and good dyeability could only be produced successfully by using chitin-chitosan adjusted its DAC ratio to 15 to 75%, preferably 18 to 70% and most preferably 25 to 70% by applying pre-immersion and post-immersion steps according to this invention.

(c) In the compression step after the pre- and post-immersion steps in the alkaline solution, the temperature of the system may be at room temperature or more or, alternatively, it may be below room temperature. However, when the temperature range of the compression step is adjusted to that of the post-immersion step, a desirable compression can be accomplished. A good viscose can be produced by adjusting the concentration of chitin-chitosan and by using a suitable amount of CS_2.

(d) The final amount of alkaline incorporated into chitin-chitosan can be adjusted by applying the pre-immersion and post immersion steps according to this invention. In the succeeding step, CS_2 reacts with chitin-chitosan at the point where the alkaline attaches. The reaction may be controlled depending on the nature of the viscose desired by adjusting the amount of the alkaline adduct at a suitable temperature. The temperature at the compression step is adjusted to that of post-immersion step in the range of 70 to 30°C depending on the nature of the viscose.

The viscose solubilized by using crashed ice may be spinned in a suitable spinning bath, or it may be used as a spinning dope in which the viscose is mixed with a cellulose viscose. The mixing may be adjusted depending on the purpose of the final product by a variety of methods. The methods of mixing to form a spinning solution may be selected from the following steps; the chitin material and a cellulose pulp is mixed and the mixture is subjected to the steps from the alkaline immersion step to the sulphidation and solubilization step to form a viscose; a mixture of an alkaline chitin-chitosan and an alkaline cellulose is subjected to the sulphidation and solubilization step to form a viscose; the chitin-chitosan xanthate and cellulose xanthate are mixed and solubilized; or a chitin-chitosan viscose and cellulose viscose are mixed together. By selecting the mixing methods described above, articles such as fibers, knits and textiles, films, nonwoven fabrics or foam materials having bio-compatibility, excellent anti-microbial property and good dyeability can be produced.

(1) Selection of the material

Chitin has a widespread occurrence in nature as structural materials mainly in arthropoda, annelida or mollusk, especially in the exo-skeleton of arthropoda. The chitin material used in this invention occurs from the legs of a species of crabs (Beni-zuwaigani) which were crushed into a fine powder followed by treatments with dilute hydrochloric acid and NaOH solution for a short time to remove calcium, proteins and other minor components. An example of the analytical data of the components is listed below.

water	5.0%
Ash	0.08%
Remaining proteins	0.05%
Viscosity (at 20°C)	450 CPS
Particle size	60 mesh pass

In measuring the viscosity at 20°C, a mixed solution of N,N-dimethylacetamide and lithium chloride is used with a concentration of the sample of 0.4%. Although the chitin material may not be necessarily occurred from Beni-zuwaigani, chitin occurred from that species of crab is suitable for the production of the chitin fibers according to this invention because it has a high viscosity as measured by the method described above and shows a high chemical and physical stability probably due to its tight glycosidic linkage. The fewer the amount of ashes and remaining proteins is the quality of the fiber obtained is more improved, wherein the amount of 0.1% or less of the remaining proteins is preferable. while viscosity has a close relation to the nature of the fiber obtained, it can be selected to a desired value in the mixed spinning with the cellulose viscose depending the mixing ratio of cellulose. Particle size correlates with the time necessary

for converting chitin to alkaline chitin and progress of de-acetylation reaction in the immersion steps described below. The preferable particle size is 4 mm or less. Although the composition and property of the commercially available chitin materials change widely as described above, those having an ash content of 0.2% or less, a viscosity of 20 to 250 CPS as measured at 30°C by using 0.4% solution in N,N-dimethylacetamide/LiCl = 96/4 and particle size of 4mm or less give preferable results and those having the values out of above standards make the industrial production difficult. DAC ratio of the chitin commercially available for industrial materials is in the range of 0.5 to 10%.

(2) Pre-immersion step

In the prior art, the immersion step in the aqueous NaOH solution was carried out at the lowest temperature possible because the purpose of this step was different from that according to this invention. The inventors of this invention, however, use an aqueous solution of NaOH with a concentration of 30 to 48% by weight and apply the immersion step at a high temperature range of 40 to 95°C to adjust the DAC ratio depending on the production purposes. Immersion at an unprecedented high temperature range enables a sufficient addition reaction of chitin with an alkali to proceed as described below by loosening the chitin structure besides making it possible to select a desirable DAC ratio. The selection of the immersion conditions depends on the materials used, the quality of the expected viscose and the chitin-chitosan ratio in the final products. Using an alkaline solution of high concentration and treating at a high temperature for a long time increase the chitosan content.

(3) Post-immersion step

The sulphidation step starts only when an alkaline attaches to chitin-chitosan. Since the addition of alkaline depends on the temperature, the temperature is selected to meet the conditions described in (4) so that a desirable alkaline addition in the succeeding steps is realized after the treatment described in (2) to proceed to the compression step. The upper and lower limits of the temperature for realizing a suitable property for the dissolution step are 70°C and 30°C, respectively, according to this invention. Actually, this upper and lower limits are regulated by the compression step described below.

(4) Compression and crushing step

Among the various compression methods, the most simple and reliable method is dehydration by centrifugation. In the rayon industry, a pressing method by passing through compression rollers is used. In the case of chitin-chitosan, compression is rather difficult as compared with the case of cellulose because the native configuration of chitin-chitosan molecule is different from that of cellulose and hydrogen bonds in chitin-chitosan are very strong, besides chitin-chitosan itself has a higher affinity against aqueous NaOH solution than that of cellulose. An adjustment of chitin-chitosan concentration or alkaline concentration would be difficult in the viscose if the problems described above are not solved. It was one of the problem to develop a method for overcoming the difficulty in chitin-chitosan production in an industrial scale, which have been solved by the inventors by controlling the temperature at the compression step. The results of the study by the inventors made it clear that the temperature at the compression step is important to achieve a best performance even when any of the several compression methods is used. The lower limit of the compression temperature is practically room temperature while the preferable temperature is 30 to 67°C.

(5) Sulphidation step

Xanthogenation reaction is carried out, under a similar condition as in the case of the production of cellulose viscose, by adding 30 to 80% by weight of carbon disulfide at a reduced pressure to the chitin material at a temperature of 20 to 35°C, followed by stirring for at least 2 hours. Although the amount of addition of carbon disulfide depends on the reaction condition and the size of the reaction vessel, it is usually adjusted to a range of 30 to 80% by weight. When the amount is less than 30% by weight, solubility of xanthate obtained is not so good while the amount of the addition of more than 80% by weight can not be applied in the process according to this invention because all the carbon disulfide added is not necessarily used effectively and sometimes causes super sulphidation.

(6) Solubilization step

Usually 2.5 to 30 holds of crashed ice against xanthate is added depending on the nature of the viscose to be produced and the mixture is stirred for 2 hours or more, preferably 2 to 15 hours, to dissolve completely. The mechanism of dissolution is that the melting point decreases in the presence of ice, water and NaOH and hydrogen bonds in the alkaline chitin-chitosan are loosened to achieve resolution. However, the dissolution is practically made difficult when the added amount of ice is less than 2.5 holds of the xanthate. As for the upper limit, the addition of ice of more than 30

holds of xanthate is not preferable since the viscose is too diluted together with causing a over-dilution of NaOH.

(7) Filtration and ripening step

The filtered viscose prepared by the similar process in the conventional cellulose viscose or a mixed viscose of chitin-chitosan viscose and cellulose viscose by one of the afore-described mixing methods is homogenized and is subjected to a ripening step to reach to an adequate viscosity for spinning, film application or molding.

Examples

This invention is further illustrated referring to the examples, although they do not limit in any sense the scope of the invention.

Example 1

In the immersion step, 40% of an aqueous NaOH solution was applied against various kinds of chitin materials at 60°C for 3.5 hours and the mixture was compressed and filtered to form an alkaline chitin-chitosan with a chitin-chitosan concentration of 27% and NaOH content of 32%. To alkaline chitin-chitosan was added 40% by weight of carbon disulfide against chitin and the mixture was allowed to react for 3 hours at 26 to 30°C. The properties of the viscose prepared by adding 12 holds of crashed ice against chitin are listed below.

No. of Experiment	No. 1	No. 2	No. 3	No. 4
Particle size	less than 1mm	less than 1mm	less than 1mm	4mm
Ash content	0.0%	0.88%	0.04%	0.19%
Viscosity of the solution (DMAC-LiCl)	67 sec	71 sec	825 sec	70 sec
Kw	890	13,700	-	39,500
No. of unreacted particles	small	large	mal-dissolution	large
DAC ratio	55%	59.5%	-	56.5%

Example 2

In this example, the same chitin material as in Example 1 was used while the conditions for preparing the slurry was changed. The material was solubilized by using 10 holds by weight of crashed ice against the chitin material and by stirring for 2 hours. The experimental results are listed below.

No. of experiment	No. 5	No. 6	No. 7	No. 8
Immersion temp.	60°C	40°C	25°C	70°C
Concentration of NaOH for immersion	41%	40%	41%	45%
Time	3 hrs	1 hr	3 hrs	3 hrs
Compression temperature (560G)	55°C	39°C	25°C	70°C
Kw	890	1,200	Unable to detect	Unable to detect
No. of unreacted	small	small	mal-dissolution	large
DAC ratio	57%	32%	5%	80%

Example 3

23g of the chitin-chitosan viscose produced by the process according to Example 1 (chitin-chitosan content: 5%) was added into 240g of a cellulose viscose (cellulose content: 9%) produced by the conventional method and mixed with stirring. After mixing thoroughly and homogeneously and de-foaming, the viscose obtained was spinned by the conventional spinning method for the viscose fibers to obtain composite fibers of chitin-chitosan and rayon. The characteristic values of the fibers obtained are listed below.

Dry strength	2.6 g/d	Dry elongation	17.0%
Wet strength	1.6 g/d	Wet elongation	23.7%

Anti-microbial activity (shake flask method)		
Staphylococcus aureuse;	degree of sterilization	53%
Bacillus pneumoniae;	degree of sterilization	88%
Pseudomonas aeruginosa;	degree of sterilization	45%

Example 4

Into 30g of No. 1 chitin-chitosan viscose (chitin-chitosan content: 5%) prepared in Example 1 was added 30g of neutral anhydrous sodium sulfate having a mean particle size of 3mm and the solution was mixed homogeneously. The mixture was placed into a vessel made of wood to form a layer of 20mm in thickness, followed by a solidification by heating with an electric current or by placing into a hot water bath. The solid obtained was placed into a spinning bath used for producing the conventional cellulose viscose fiber containing 1 litter of spinning solvent and the bath was heated to reflux for about 1 hour. After the reflux, the remaining solid was washed with warm water and then with an aqueous NaOH solution on 3% by weight in concentration. After a bleaching step, a sponge like solid was obtained. This sponge-like product had an apparent specific gravity of 0.34 and was highly hygroscopic.

Example 5

The No. 5 or No. 6 viscose produced in Example 2 was mixed with a conventional rayon viscose to adjust the proportion of the chitin-chitosan fiber of the final product to 10% by weight. The fiber spinned in a conventional spinning bath for rayon was formed into nonwoven fabrics. Determination of degree of sterilization by a shake flask method as regulated by Committee of Anti-microbial and Deodorant Finishing for Textile, Japan (Seni Seihin Eisei Kakoh Kyougikai: SEK) showed higher effects in the products having higher DAC ratio.

Degree of sterilization	
No. 5 (DAC ratio: 57%)	94%
No. 6 (DAC ratio: 32%)	48%
E. coli IFO No. 3301 was used for the test bacteria.	

Effect of The Invention

(a) According to the present invention, a viscose of chitin-chitosan can be produced by using conventional viscose production facilities with some improvements in cellulose viscose production process. From this chitin-chitosan vis-

cose were produced, after mixing with a cellulose viscose by the various mixing method described hitherto, chitin fibers, chitin films or sponge like solids that can be applied for various use. Industrial production of chitin-chitosan viscose was made possible from the commercially available chitin material by adjudging its degree of polymerization in the immersing step, by adjusting its DAC ratio depending on the final use of the product or by controlling the temperature of the alkaline solution at the compression step.

(b) Chin-chitosan can be arbitrarily mixed with cellulose in their raw materials or in the steps of alkaline addition, xanthate formation or viscose formation.

(c) The chitin-chitosan fibers or films according to this invention are especially excellent in their anti-microbial activity. As are shown in Example 3, the chitin-chitosan and natural rayon mixed fibers showed a degree of sterilization of 53% for Staphylococcus aureuse, 88% for Bacillus pneumoniae and 45% for Pseudomonas aeruginosa before washing, which are the values that meet well to the standards of SKE (not less than 26%).

(d) Besides anti-microbial activity, the chitin-chitosan fibers or films, or complexed fibers or films of chitin-chitosan and cellulose, are useful for their better dyeability to acidic dyes by taking advantage of the cationic nature of chitin-chitosan as compared with the fibers or films obtained from the conventional cellulose viscose. This cationic nature is applicable, not only for fibers having dye affinity, but also for fibers having various chemically capturing activity (absorptivity or reactivity).

(e) The Chitin-chitosan fibers according to this invention (having cellulose content of 0 to 100%) can be used not only by itself but also by being blended or blended and woven with natural fibers like silk, cotton, flax or wool, or regenerated fibers, man-made fibers, or synthetic fibers like polyester, nylon, acrylic fibers.

(f) The chitin-chitosan fibers or articles according to this invention can be effectively used for deodorizing materials or growth accelerating agents for plants.

(g) The chitin-chitosan/cellulose fibers or films are applicable for nonwoven fabrics, films as well as for textiles like spinning fibers, clothing or knits. The nonwoven fabrics, foam materials or films can be used for clothing like surgical wears having an anti-microbial activity, daily miscellaneous goods such as diapers having an anti-inflammation effect or wet tissue papers having an anti-microbial activities, agricultural goods like films having a soil-reforming effect, bed-mats like a cushion for preventing frictional inflammation, industrial materials like filters having an anti-microbial activity, or medical materials.

(h) The composite sponge of chitin-chitosan/cellulose according to this invention can be used for toiletries like a sponge for washing the face and body.

(i) Knits and textiles of chitin-chitosan/cellulose can be used for clothing like undershirts, socks or T-shirts, bedroom commodities like pajamas, bed covers or cushions, miscellaneous dairy goods like towels, slippers or cloth bags, or medical materials like gauzes, bandages, stapes or plasters.

Claims

1. A process for producing chitin-chitosan viscose characterized in that a chitin material containing 0.2% by weight or less of ashes, having a viscosity of 20 to 250 CPS and particle diameter of 4mm or less is used, comprising the steps of adjusting DAC ratio and degree of polymerization of said chitin material by immersing the material in 30 to 48% by weight of an aqueous solution of NaOH for 10 to 300 minutes at 40 to 95°C (referred to as a pre-immersion step) to form a compound having a structure unit of chitin having aminoacetyl groups and a structure unit of chitosan having amino groups (referred to as chitin-chitosan hereinafter), immersing the chitin-chitosan in said aqueous solution of NaOH for 10 to 60 minutes at a reduced temperature of 70 to 30°C to adjust NaOH content (referred to as a post-immersion step) and crushing the chitin-chitosan after compressing it into 3 to 5 times the specific weight of the chitin material; followed by subjecting to a xanthogenation reaction of chitin-chitosan by introducing 28 to 80% by weight of CS_2 to the chitin material at 20 to 35°C for 2 to 4 hours at a reduced pressure, and then adding 2.5 to 30th volume of crushed ice to the chitin material to dissolve the chitin-chitosan with stirring for 2 to 30 hours.

2. A process for producing a fiber of chitin-chitosan alone or a fiber composed of chitin-chitosan and cellulose, characterized in that the fiber is spinned by the wet spinning method for the conventional viscose rayon by using a viscose containing chitin-chitosan alone produced by the steps according to Claim 1, or by using a viscose in which a viscose of cellulose is solubilized in a desired amount.

3. A process for producing chitin-chitosan films or chitin-chitosan and cellulose complexed films, characterized in that the films are formed by a conventional viscose process for producing cellulose films using a viscose of chitin-chitosan alone produced according to the steps in Claim 1 or using a viscose in which chitin-chitosan and cellulose are solubilized in a desired ratio by weight followed by defoaming.

4. A process for producing foam materials of chitin-chitosan or mixed foam materials of chitin-chitosan and cellulose,

characterized in that the chitin-chitosan viscose, which is produced by the steps according to Claim 1 or a viscose produced by the process according to Claim 2, in which the chitin-chitosan and conventional cellulose are solubilized in a desired amount, is mixed with a foaming agent (a bubble forming agent) and spinned in a spinning bath for the cellulose viscose to produce the foam materials.

5. Chitin-chitosan fiber or chitin-chitosan and cellulose mixed fiber, knits and textiles, film, nonwoven fabric or foam material, characterized in that fibers, films or foam materials composed of chitin-chitosan or chitin-chitosan and cellulose produced by the process according to Claim 2, 3 or 4 are used for clothing, medical articles, hygienic articles or miscellaneous daily goods having bio-compatibility, anti-microbial activity and good dyeability.

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(54) Process for producing articles of regenerated chitin-chitosan containing material and the resulting articles

(57) The present invention provides fiber materials, knits and textiles, nonwoven fabrics, miscellaneous daily goods or foam materials having an improved dyeability, bio-compatibility, anti-microbial activity, good biodegradative property, and being effective for deodorizing uses, growth enhancing uses for plants and medical uses, and having anti-microbial effect produced from the chitin-chitosan viscose which is produced by a xanthogenation reaction of alkaline chitin-chitosan having a different DAC ratio through a pre- and post-immersion steps in an NaOH solution, or from a viscose in which chitin-chitosan and cellulose are solubilized.

In the process for producing chitin-chitosan/cellulose fibers, films or foam materials from the chitin-chitosan/cellulose viscose, chitin-chitosan in which DAC ratio and degree of polymerization are adjusted is formed through an improved pre-immersion step in which the chitin material is immersed in a NaOH solution of high concentration at high temperature and through an improved post-immersion step in which the temperature is decreased. The chitin-chitosan/cellulose viscose is produced by a xanthogenation reaction with CS_2 and by dissolving in crashed ice. The viscose obtained or a viscose in which chitin-chitosan and cellulose are solubilized in a desired ratio is used for producing fibers or films, and the viscose in which a foaming agent is added is used for producing foam materials. Span-lace process nonwoven fabrics can be also produced from these viscose.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	US 2 202 003 A (HASKINS J F) * the whole document *	1-5	C08L5/08 C08L1/02 D01F9/00 C08J5/18 C08J9/00 C08B37/00 C08B9/02 //C08L5:08, C08L1:02
Y	US 2 217 823 A (THOR C J B) * the whole document *	1-5	
D,P, Y	PATENT ABSTRACTS OF JAPAN vol. 096, no. 008, 30 August 1996 & JP 08 092820 A (OMIKENSHI CO LTD;KOYO CHEM KK), 9 April 1996, * abstract *	1-5	
Y	US 2 040 879 A (RIGBY G W) * the whole document *	1-5	
A	US 5 320 903 A (HIRUKAWA T ET AL) * column 1, line 15 - line 29 *	1-5	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C08B
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Place of search	Date of completion of the search	Examiner
THE HAGUE	13 February 1998	Tarrida Torrell, J

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